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**Silver Migration and Transport Mechanism Studies**

in

**Silver Oxide-Zinc Batteries**

**Contract No. AF 33 (657) -8689**

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Department of Chemistry

CALVIN COLLEGE

Grand Rapids Michigan

Silver Migration and Transport Mechanism Studies

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## FOREWARD

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## ABSTRACT

A study has been made of three methods whereby radioactive silver can be used to determine quantitatively the concentration of small amounts of silver dissolved in potassium hydroxide solutions. Good results were obtained by precipitating the dissolved silver as silver iodide and collecting this on a filter paper of sufficiently small pore size. The precipitated silver iodide was then counted.

## I. INTRODUCTION

One of the drawbacks to the more widespread use of silver-zinc-alkali batteries is the fact that the silver oxides are soluble in the KOH electrolyte. Because of this, silver can be transferred to the zinc plates of the battery and eventually cause internal shorting. This transport of silver can be, and is, lessened by the use of separator materials. However, after cells have been cycled for some time there are likely to be extensive silver deposits on or in the separators. If these deposits build up they also can lead to internal shorting.

A large variety of materials has been tested and tried as separator material in silver-zinc cells. Combinations of materials have also been used, but no completely satisfactory material has been found. The purpose of the work under this contract is to study the transport mechanism of silver in the silver-zinc or silver-cadmium cells, with the hope that such a study may uncover some of the significant requirements of an ideal separator in an alkaline battery using silver electrodes.

One of the methods of following this migration of silver used radioactive silver isotopes. During the past quarter a study has been made of methods for using these radioactive silver isotopes as a means for quantitatively determining the amount of silver dissolved in the electrolyte.

## II. EXPERIMENTAL

### A- General Procedure.

Solutions of  $\text{Ag}_2\text{O}$  in KOH containing  $\text{Ag}^{110}$  as a tracer were prepared and the ratio between concentration and counting rate was determined. Concentration was measured by potentiometric titration with KI as described in the previous Quarterly Technical Progress Report and the counting rate was measured by means of a Geiger tube. The concentration values were reproducible to within 1% and were assumed to be the correct values. After reducing the silver concentration by dilution or chemical action the titration and counting were repeated. If the ratio between concentration and counting rate is constant over a range of concentrations the method may be considered quantitative.

### B- Preparation of the Tracer Solution

Excess solid  $\text{Ag}_2\text{O}$  was added to 30% KOH solutions and stirred with a magnetic stirring device for one hour. The solution was filtered through a fine Pyrex glass frit and 0.1 microcurie of  $\text{Ag}^{110}$  was added to 100 ml of solution. The specific activity of the  $\text{Ag}^{110}$  sample was 100 millicuries per gram of silver.



### III. RESULTS

Three different methods were used to prepare the sample for counting.

Method I. The original solution was divided into four parts and then three samples were diluted with different amounts of 30% KOH. A 10 ml. portion of each solution was analyzed by potentiometric titration with KI and a 0.5 ml. sample was placed in a ringed steel planchet, dried under a heat lamp, and counted. The results are tabulated in Table I. The values in column 4 show that this method does not give quantitative results.

TABLE I

Comparison of titration with Counting  
method on KOH-Ag<sub>2</sub>O solutions using  
METHOD I

Sample	Molarity x 10 <sup>4</sup>	Activity Counts/min.	Ratio Conc./activity
1	4.77	228	2.09 x 10 <sup>-6</sup>
2	2.20	131	1.68 x 10 <sup>-6</sup>
3	1.22	75	1.63 x 10 <sup>-6</sup>
4	1.03	102	1.01 x 10 <sup>-6</sup>
5	1.03	93	1.11 x 10 <sup>-6</sup>

The deviation from quantitative behavior and the lack of reproducibility are likely due to the fact that KOH crept over the side of the planchet during the drying process and absorbed water rapidly while in the counter well. The samples were counted about 20 - 30 minutes and the absorption of water resulted in an appreciable decrease in measured activity with increasing time.

Because of this difficulty, no further work was done with this method.

Method II. An attempt was made to eliminate the undesirable characteristics of Method I by neutralizing the KOH with  $\text{HNO}_3$  before drying and then counting the solid sample of  $\text{KNO}_3 - \text{Ag}^{110}$ .

One ml. of 30% KOH- $\text{Ag}^{110}$  solution was neutralized by the addition of 0.5 ml of concentrated nitric acid. The hot solution was stirred, 1 ml. of it was transferred to a planchet and dried under a heat lamp.

Four 1 ml. samples of  $\text{KNO}_3 - \text{Ag}^{110}$  were prepared from a 30% KOH solution which was  $1.27 \times 10^{-4}$  M with respect to dissolved silver. The volume of  $\text{KNO}_3$  produced was large and there was some creeping of the  $\text{KNO}_3$  over the edge of the planchets. However, slow drying of the salt produced a rather uniform distribution of the salt and kept creeping at a minimum. The results obtained are given in Table II.

TABLE II

Reproducibility of Counting of dried  
 $\text{KNO}_3 - \text{Ag}^{110}$  Residues.

<u>Sample</u>	<u>Counts/min.</u>
1	123
2	123
3	118
4	126

These results show that there is some variation but it was felt that more work on this method was justified.

Two different solutions of  $\text{Ag}_2\text{O}$  dissolved in 30% KOH were prepared, placed in a flask, and allowed to stand. During this stand the  $\text{Ag}_2\text{O}$  decomposed. The decrease in dissolved silver was then determined by filtering the solutions at intervals, neutralizing samples with nitric acid as described above, and counting. Samples were also titrated with KI at the same time to determine the "true" concentration of dissolved silver. The results are summarized in Table III and on Figure 1. The results are not considered acceptable because the lines, Fig. 1, are not parallel and do not go through the origin.

TABLE III

Comparison of Counting with Titration Methods  
for KOH-Ag<sub>2</sub>O Solutions using Method II

Solution A		Solution B	
Concentration by titration	Activity	Concentration by titration	Activity
M x 10 <sup>4</sup>	counts/min.	M x 10 <sup>4</sup>	Counts/min.
4.97	215	5.0	194
2.5	142	2.8	138
2.4	143	2.0	127
1.0	71	1.0	70
1.0	72	1.0	70

Another variation was then used in an effort to decrease the quantity of KNO<sub>3</sub> on the planchet and thus decrease the amount of self absorption of the radiation. The neutralized solution was cooled to a temperature at which much of the KNO<sub>3</sub> precipitated. 0.5 ml of the liquid was then placed on a planchet and dried. There was less KNO<sub>3</sub> and it was more uniformly distributed, but the variation in the activities of the two samples tested was large--54 and 38 counts per minute. This indicated that some of the Ag<sup>110</sup> was lost by occlusion on the precipitated KNO<sub>3</sub>.

On the basis of all these results, this method too was abandoned. It should be noted that the time involved in sample preparation, drying, and counting was at least as long as in the potentiometric method of analysis, so no advantage would be gained even if the method was accurate.

Method III. A 1 ml. sample of the 30% KOH-Ag<sub>2</sub>O solution was diluted with 1 ml. of water to prevent crystallization of KNO<sub>3</sub>. The solution was then made acid by the addition of 0.5 ml. of concentrated nitric acid. Ten drops of  $1 \times 10^{-2}$  M KI were added to precipitate the dissolved silver as AgI. The AgI was collected on a millipore filter paper. The filter paper was then placed on a planchet and counted. A small lead ring was placed around the edge of the filter paper in the planchet to keep the paper from wrinkling as it dried out. The results are given in Table IV and On Figure 2.

TABLE IV

Effectiveness of Counting Using Pre-  
cipitated Silver Iodide.

Sample	Concentration M x 10 <sup>4</sup>	Counts/minute	
		Method II	Method III
1	4.4	175	195
2	3.0	144	116
3	1.9	109	78
4	1.3	—	65
5	0.6	—	63

These results show that there is better correspondence between concentration and counting by Method III than by Method II, but still it is not good enough to be considered quantitative. However, it was noted that considerable activity was present in the filtrate from the samples. Thus not all the AgI was collected on the filter paper. This was also noted in two other cases where Method III was used, Figure 3. At zero counts/minute there was still some silver dissolved in the KOH solution. This supports the suggestion that some AgI is lost through the filter paper.

To check this point another series of runs was made similar to those above except that the solution containing the precipitated AgI was filtered twice through the same piece of filter paper instead of once. The results are given in Table V and on Figure 4.

TABLE V

Comparison of Titrimetric Method with  
Counting of Silver Iodide Precipitates

Moles of $\text{Ag}^+ \times 10^7$	Activity Counts/minute
44	3000
8.8	776
4.4	378
2.2	180
0.88	72
0.44	36

Here there is excellent agreement between the amount of dissolved silver and counting rate for all except the largest sample which is not shown on Figure 4. This may be due to self absorption by the relatively large quantity of AgI on the filter paper.

The filter paper used in these experiments had a pore size of 1.20 microns. Since significant amounts of AgI passed through the paper, requiring double filtration, it was decided to investigate the possibilities of using filter paper of smaller pore size. Two advantages could be gained: (a) the AgI could be removed in one filtration, and (b) the activity of the sample should be greater. The filter paper selected had a pore size of 0.2 micron and the solutions from which the AgI was precipitated were filtered only once, and then the precipitate was counted. The results are given in Table VI and on Figure 5.

TABLE VI

Counts of Silver Iodide Precipitate  
using fine pore filter paper

Concentration $M \times 10^4$	Counts/minute
4.8	570
2.4	285
1.6	187
0.96	133
0.69	81
0.48	55

The results again show that this method can be used to analyze KOH solutions quantitatively for small quantities of dissolved silver.

#### IV. CONCLUSIONS

Small concentrations of silver dissolved in KOH can be determined quantitatively using radioactive silver as a tracer. Good results have been obtained by precipitating the silver as silver iodide, filtering, and then counting as described in Method III above. This method is particularly sensitive and accurate at low concentrations of silver, where the potentiometric method gives the least precise results. However, in using this method it is necessary to run a calibration by determining the concentration of silver in one solution by means of the potentiometric method.

#### V. PROGRAM FOR NEXT QUARTER

Measurements of radioactivity in the electrolyte will be made directly during the cycling of a silver-cadmium cell. This will be done in a further effort to determine the nature of silver migration in a working cell. In these cells the silver electrode will be made by plating radioactive silver on a small nickel screen.

VI. CAPTIONS FOR FIGURES

Figure 1. Radioactive count of  $\text{KNO}_3\text{-Ag}^{110}$  residues vs. concentration of dissolved  $\text{Ag}_2\text{O}$ .

Figure 2. Effect of filtration on counting of AgI precipitates.

Figure 3. Counts of AgI vs. concentration of dissolved  $\text{Ag}_2\text{O}$ .

Figure 4. Counts of AgI vs. concentration of dissolved  $\text{Ag}_2\text{O}$ .

Figure 5. Counts of AgI vs. concentration of dissolved  $\text{Ag}_2\text{O}$  using single filtration with small-pore filter paper.

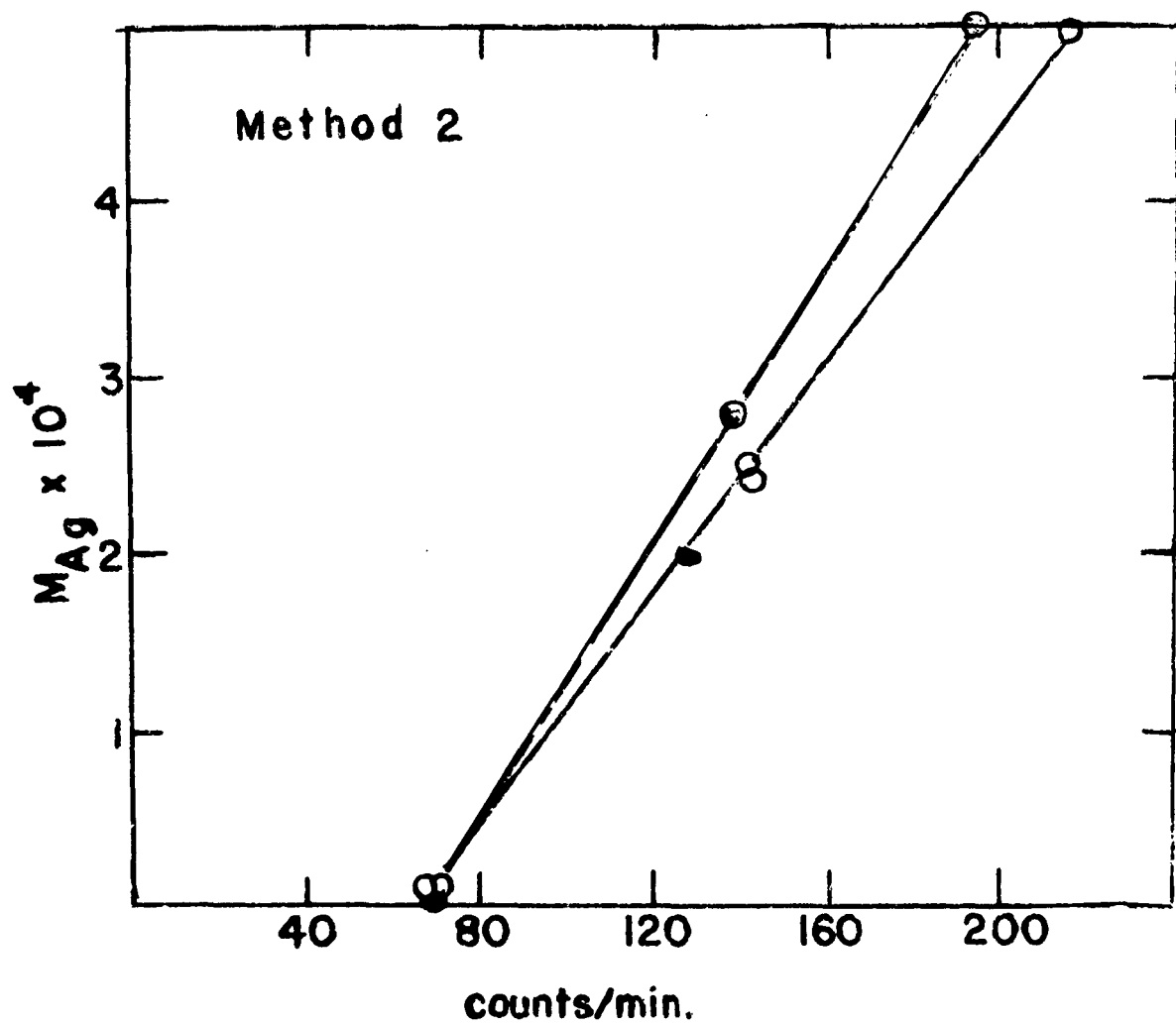


Figure 1



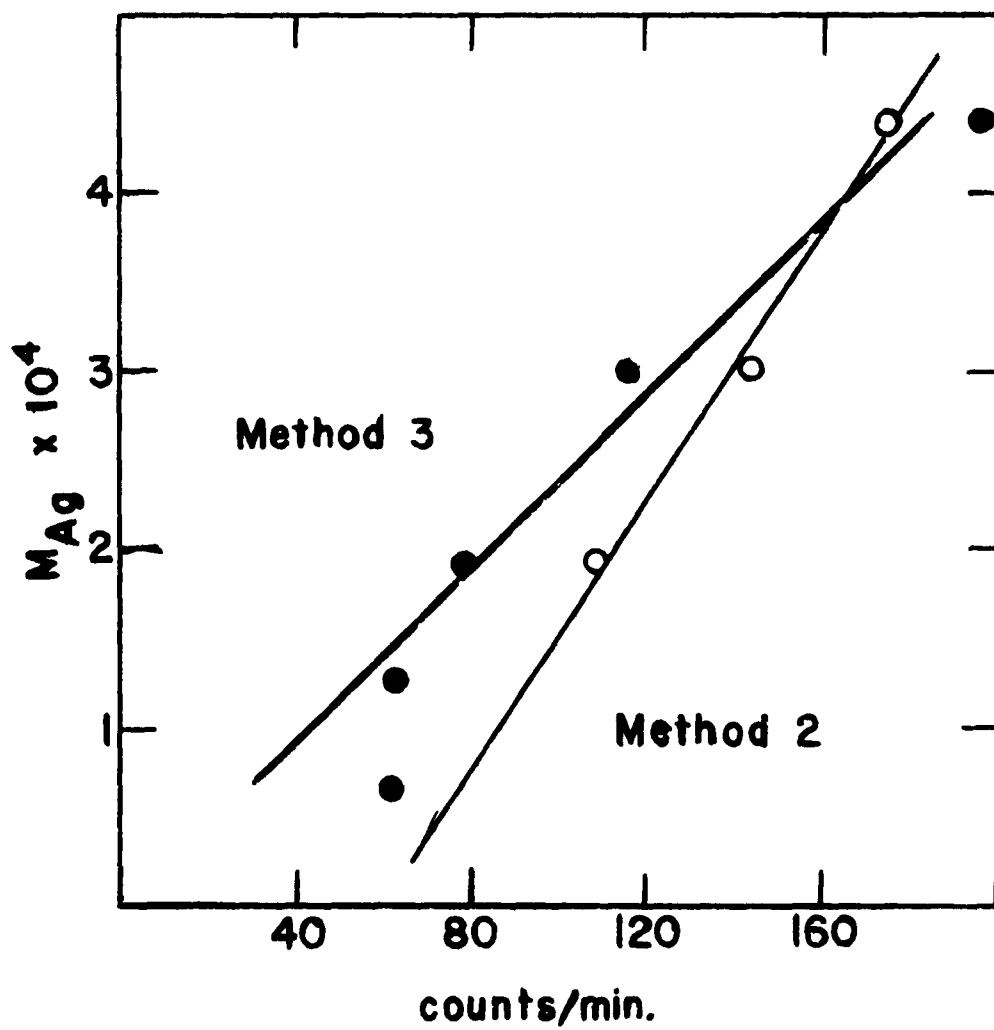


Figure 2

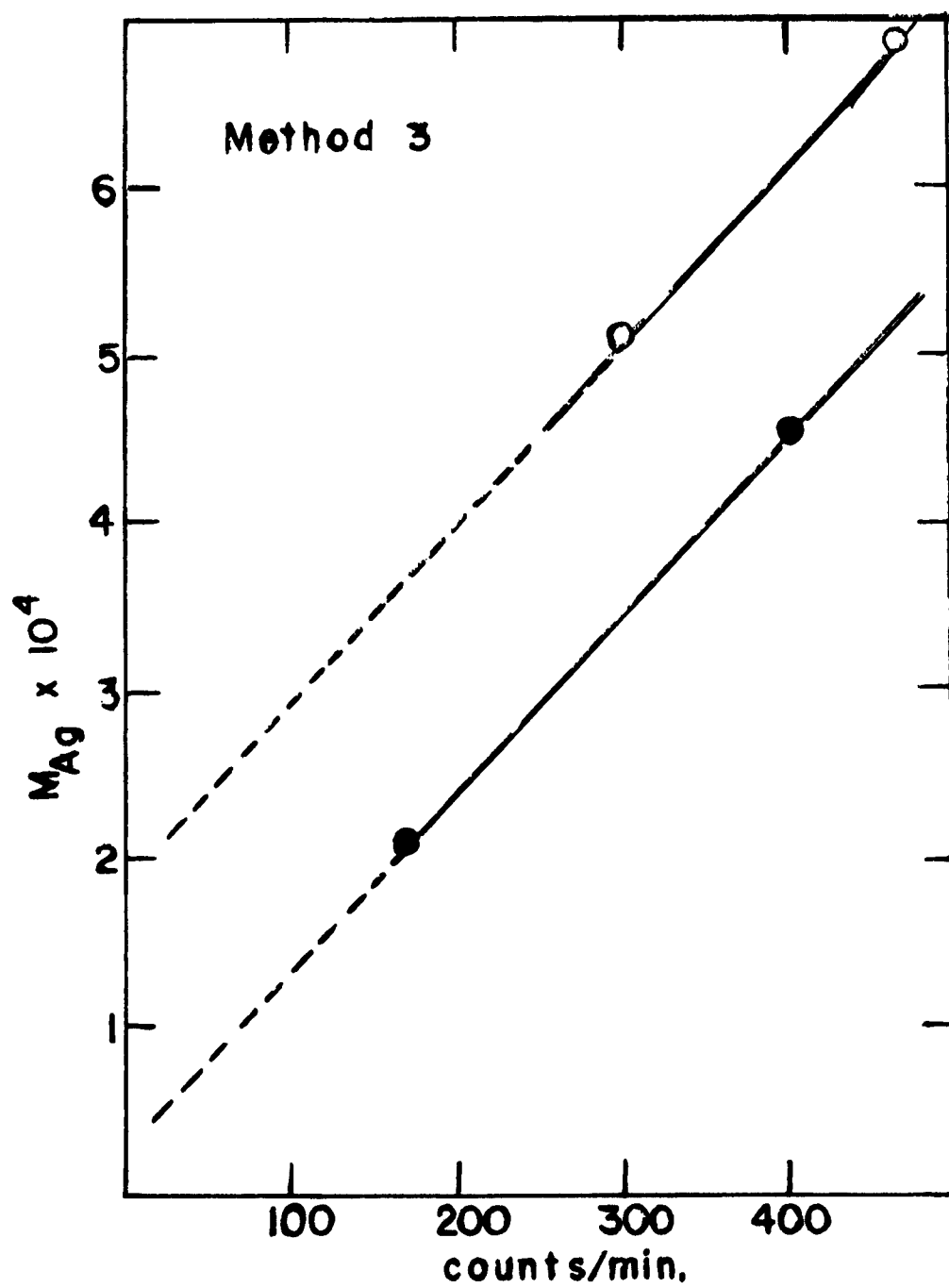


Figure 3

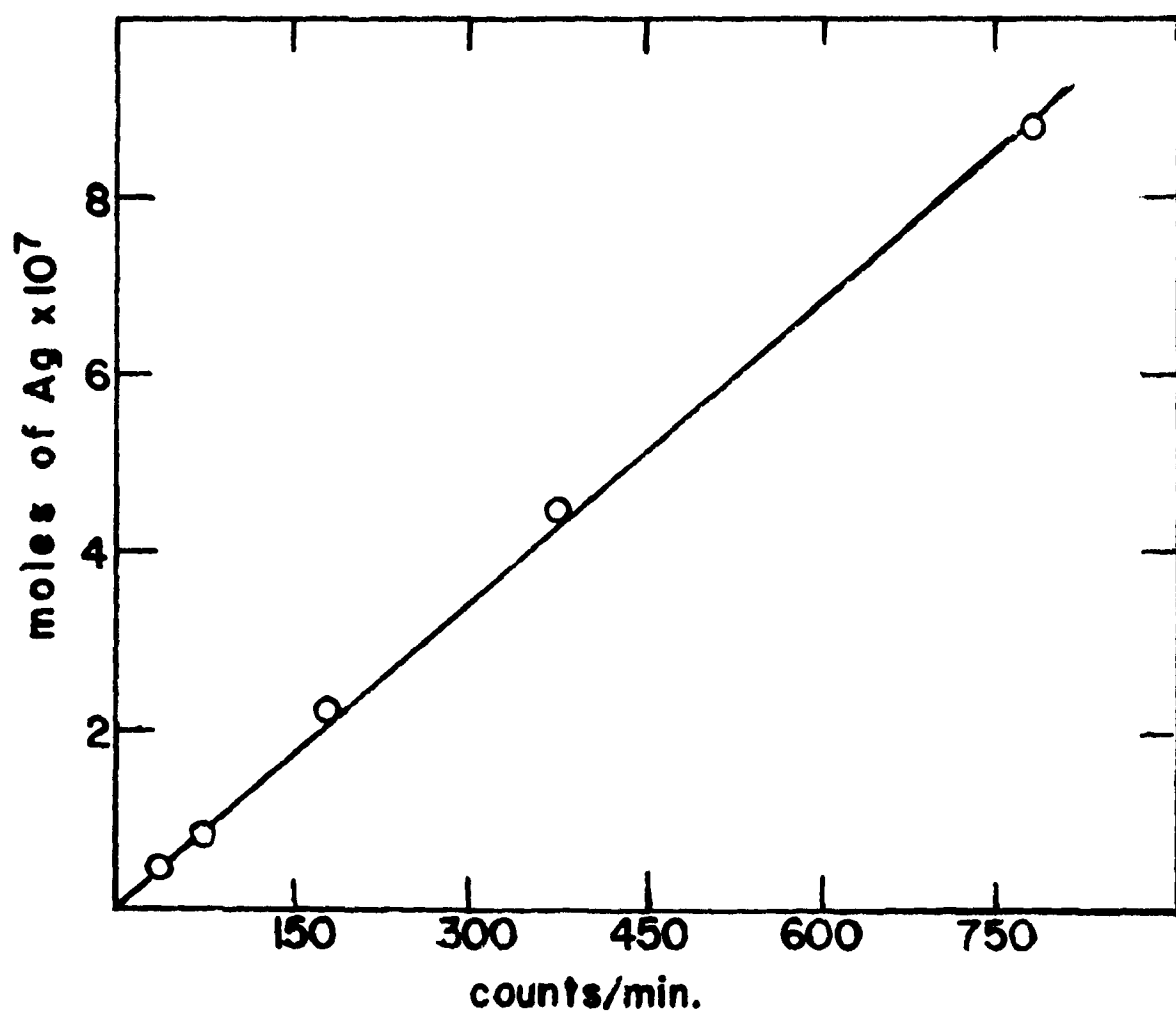
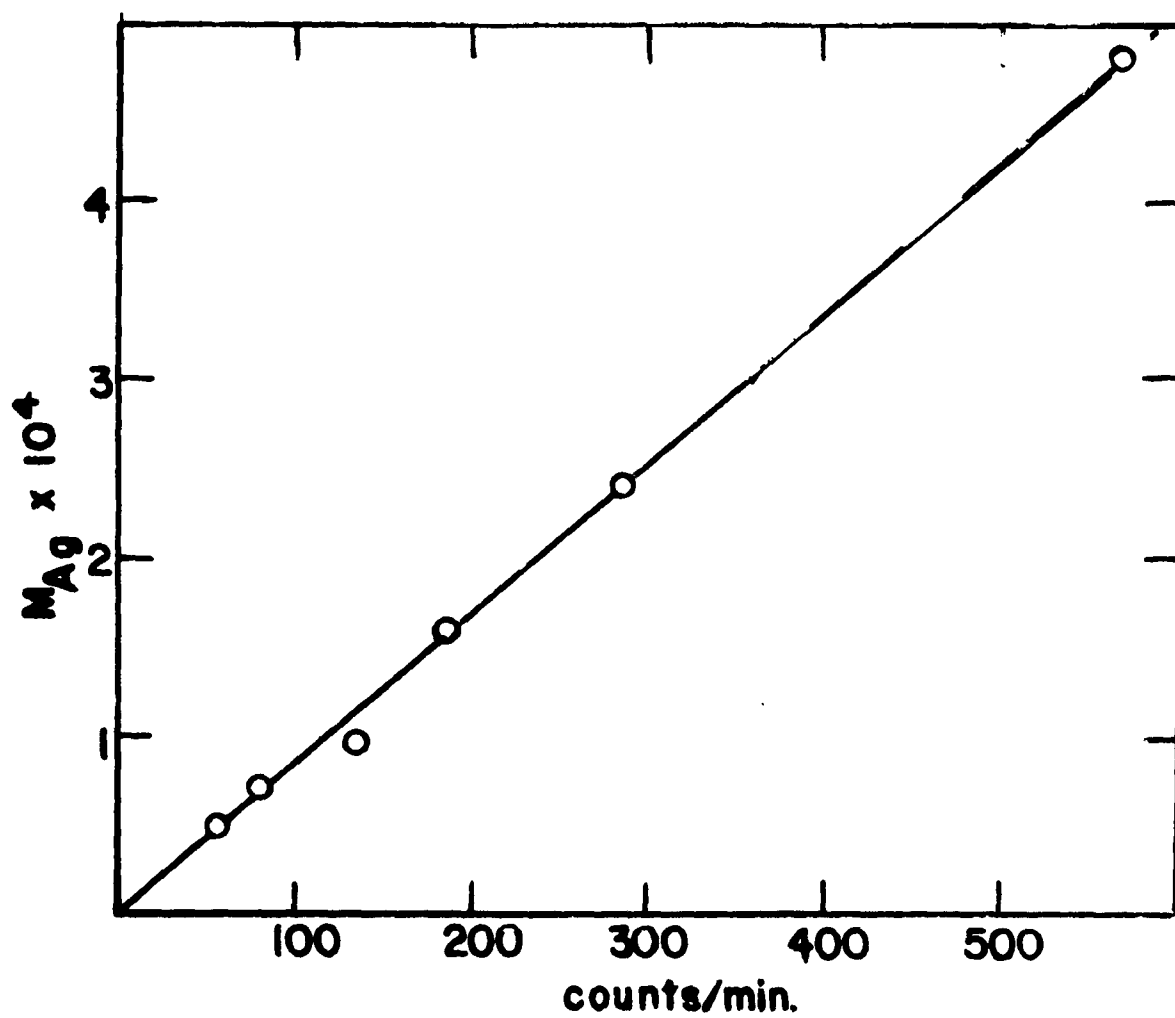


Figure 4



**Figure 5**

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